



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US94/12645 <b>(22) International Filing Date:</b> 2 November 1994 (02.11.94) <b>(30) Priority Data:</b> 08/148,110 4 November 1993 (04.11.93) US <b>(71) Applicant:</b> ALLIEDSIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US). <b>(72) Inventors:</b> UNGER, Peter, D.; 36 Terry Drive, Convent Station, NJ 07961 (US). ROHRBACH, Ronald, P.; 430 Cherryville Road, Flemington, NJ 08822 (US). <b>(74) Agent:</b> CRISS, Roger, H.; AlliedSignal Inc., (Attn: C.A. McNally, Law Dept.), 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).		<b>(81) Designated State:</b> JP.  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> LOW DENSITY MATERIALS HAVING GOOD COMPRESSION STRENGTH AND ARTICLES FORMED THEREFROM <b>(57) Abstract</b> <p>A crosslinked, highly porous body derived from a water-soluble, hydrogel polymer, wherein the porous body is characterized in that it has an open-celled 3-dimensional lattice structure, a density of less than about 1.0 g/cm<sup>3</sup>, a surface area of equal to or greater than about 30 m<sup>2</sup>/g, a compression strength of equal to or less than about 10 % yield at 10 psi, and an average pore diameter of less than about 1000 Angstroms. When the hydrogel polymer used is guar gum, the resulting product is particularly useful for thermal insulation applications.</p>		

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LOW DENSITY MATERIALS HAVING GOOD COMPRESSION  
STRENGTH AND ARTICLES FORMED THEREFROM

5                    Cross Reference to Related Applications

This application is a continuation-in-part of copending application Serial No. 27,975 filed March 8, 1993 which is a continuation-in-part of copending application Serial No. 811,757, December 20, 1991, now abandoned.

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Background of the Invention

This invention relates to novel porous bodies which possess a low density and a high surface area as well as one or more other beneficial properties such as pore volume and strength characteristics, which makes  
15 them suitable for many industrial applications, such as insulating materials, fibers, absorbents, adsorbents, ion-exchange resins, membranes and support materials for a wide variety of uses. The porous bodies have an open-celled 3-dimensional lattice structure.

Numerous attempts have been made to make low density solid  
20 materials. For instance, U.S. Pat. No. 4,110,164 to Sutthoff et al. teaches a porous granule produced by mixing a modified cellulose and a densification agent into an agglomerated fibrous ion exchange composite that may be useful in immobilizing enzymes.

U.S. Pat. No. 4,675,113 to Graves et al. discloses porous beads  
25 comprising calcium alginate and magnetite that are suitable for affinity chromatography. The porous beads are formed by dripping an admixture of alginic acid and magnetite into a calcium chloride solution. The alginic /magnetite admixture may further contain triethanolamine titanium, a crosslinking agent, to provide additional physical strength.

30            Aerogels are examples of highly porous materials. Aerogels have been made from iron and tin oxides, aluminas, tungsten, biopolymers and, more commonly, silicas. The first aerogels were produced in the early 1930's (Kistler, Stanford University) by exchanging the water in an aqueous solution of sodium silicate with an alcohol, and then removing the  
35 alcohol under high temperature and pressure (81 bars, 240°C). The aerogels have densities in the range of 0.03 to 0.3 g/cm<sup>3</sup>. Recently, Hrubesh of The Lawrence Livermore National Laboratory modified the technique by using a condensed silica form, base catalyst and supercritical

fluid extraction to achieve porous solids of silica aerogels having ultra low density of about  $0.005 \text{ g/cm}^3$  (See, Robert Pool Science, 247 (1990), at 807). One disadvantage of such materials is that at these densities the porous solids have limited strength properties. Secondly, the aerogels can be somewhat difficult to modify (chemically) for various commercial applications. Another disadvantage of the Hrubesh method is the use of the expensive supercritical fluid extraction procedure.

Others have attempted to crosslink polymeric gel materials, such as chitosan. For example, Japanese Patent Publication No. 61-133143, published June 20, 1986, and U.S. Pat. No. 4,833,237 to Kawamura et al. disclose crosslinked granular bodies derived from a low molecular weight chitosan. The process for producing the chitosan bodies comprises dissolving a low molecular weight chitosan into an aqueous acidic solution, pouring the solution into a basic solution to form porous, granular gel bodies of chitosan, thoroughly replacing the water contained in the granular gel bodies with a polar solvent, and then crosslinking the granular bodies with an organic diisocyanate. However, it has been found that the water-solvent replacement process causes a significant portion of the pores, especially fine pores, to collapse, preventing the crosslinking agent from having access to form crosslinks. Consequently, the resultant product is swellable and has significantly reduced surface area.

### Summary of the Invention

The present invention provides a crosslinked, highly porous body derived from a water-soluble, hydrogel polymer. The porous body is characterized in that it has an open-celled 3-dimensional lattice structure, a density of less than about  $1.0 \text{ g/cm}^3$ , a surface area of equal to or greater than about  $30 \text{ m}^2/\text{g}$ , and a compression strength of equal to or less than about 75% yield at 300 psi, and is derived from a polymer which is selected from the group consisting of alginates, gums, starch, dextrans, agar, gelatins, casein, collagen, polyvinyl alcohol, polyethylenimine, acrylate polymers, starch/acrylate copolymers, and mixtures and copolymers thereof. Preferably, the porous body has a compression strength of equal to or less than about 10% yield at 10 psi. Preferably, the porous body has an average pore diameter of less than about 1000 Angstroms.

The present invention also provides a powder derived from a water-soluble, hydrogel polymer. The powder has an average particle diameter

of about 1 to about 10 microns, an average pore diameter of less than about 1000 Angstroms, a density of less than about  $1.00 \text{ g/cm}^3$ , and a compression strength of equal to or less than about 10% yield at 10 psi. The hydrogel polymer is selected from the group consisting of alginates, gums, starch, dextrans, agar, gelatins, casein, collagen, polyvinyl alcohol, polyethylenimine, acrylate polymers, starch/acrylate copolymers, and mixtures and copolymers thereof

The present invention further provides a process for making a crosslinked, highly porous body comprising the steps of dissolving a hydrogel polymer in a gelling solvent, forming a gel from the dissolved polymer solution into a desired configuration, gradually replacing the gelling solvent with a crosslinking solvent by employing a concentration gradient solvent exchange process, adding a crosslinking agent to crosslink the gel, and isolating the crosslinked gel from the crosslinking solvent, wherein the porous body is characterized in that it has an open-celled 3-dimensional lattice structure, a density of less than about  $1.0 \text{ g/cm}^3$ , a surface area of equal to or greater than about  $30 \text{ m}^2/\text{g}$ , and a compression strength of equal to or less than about 75% yield at 300 psi. Preferably, the porous body has a compression strength of equal to or less than about 10% yield at 10 psi. Preferably, the porous body has an average pore diameter of less than about 1000 Angstroms.

The present invention also provides a process for making a highly porous body comprising the steps of dissolving a crosslinked, hydrogel polymer in a gelling solvent that contains an additive selected from the group consisting of surfactants, elastomeric additives, and polyols; forming a gel from the dissolved polymer solution into a desired configuration; freeze-drying the gel; adding a crosslinking solvent to the freeze-dried gel; adding a crosslinking agent to the crosslinking solvent, and isolating the crosslinked gel from the crosslinking solvent, wherein the porous body is characterized in that it has an open-celled 3-dimensional lattice structure, a density of less than about  $1.0 \text{ g/cm}^3$ , a surface area of equal to or greater than about  $30 \text{ m}^2/\text{g}$ , and a compression strength of equal to or less than about 75% yield at 300 psi. Preferably, the porous body has a compression strength of equal to or less than about 10% yield at 10 psi. Preferably, the porous body has an average pore diameter of less than about 1000 Angstroms.

The present porous bodies exhibit numerous beneficial properties including low density and high surface area as well as high pore volume

and excellent strength characteristics. In addition, the porous bodies have excellent dimensional stability even after thorough dehydration and rehydration, especially at high levels of crosslinkage in such levels that are not possible to accomplish using the prior art solvent exchange processes.

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#### Brief Description of the Drawings

Figure 1 is a schematic drawing which depicts a porous body of this invention and its open-celled 3-dimensional lattice structure.

Figure 2 is a graph of the results obtained in Example 2.

10 Figure 3 is a graph of the results obtained in Example 6.

Figure 4 is a graph of the results obtained in Example 7.

Figure 5 is a graph of the results obtained in Example 8.

Figure 6 is a graph of the results obtained in Example 9.

15 Figure 1 depicts a section of the open-celled 3-dimensional lattice of a porous body of this invention. The porous body 10 has pores 11, which form a continuous network of pores.

#### Detailed Description of the Invention

20 As mentioned above, the present invention provides highly porous, high-strength crosslinked bodies derived from hydrogel polymers. Hydrogel polymers are water soluble polymeric materials that absorb water to form free-flowing gel-like substances, pregels. The pregels are set or coagulated to form porous gels that are free-standing, and then  
25 crosslinked with an appropriate crosslinking agent to form the high-strength porous bodies of the present invention. The porous hydrogel bodies have a 3-dimensional open-celled lattice structure, for example, as illustrated in Figure 1. The term lattice as used herein refers to an open framework of crosslinked polymer.

30 The porous hydrogel bodies of the present invention have a low density of less than about  $1.0 \text{ g/cm}^3$ , preferably less than or equal to about  $0.5 \text{ g/cm}^3$ , more preferably less than or equal to about  $0.3 \text{ g/cm}^3$ , and most preferably less than or equal to  $0.2 \text{ g/cm}^3$ . In other preferred embodiments, the density is equal to or less than  $0.15 \text{ g/cm}^3$ , and more  
35 preferably less than about  $0.1 \text{ g/cm}^3$  or even less than about  $0.05 \text{ g/cm}^3$ . However, preferably, the bodies have a minimum density which is at least sufficient to maintain the 3-dimensional lattice structure of the body. In many preferred embodiments of the invention, the bodies have a density of

at least about  $0.01 \text{ g/cm}^3$ , and preferably at least  $0.02 \text{ g/cm}^3$ .

The novel porous bodies of this invention also have excellent surface area characteristics, which can play a substantial factor in the utility of porous bodies and articles formed therefrom. For example, their high exposed surface area, higher than that of other available materials, is available for attachment or adsorption of active agents and the like. An increase in surface area per unit weight of a material often minimizes the amount of material needed to perform a desired function. For example, the ability of a given amount of a material to perform as an adsorbent can be viewed as a function of the amount of adsorption per unit weight of the material. The more surface area per unit weight, the better the material will function as an adsorbent.

The present porous open-celled 3-dimensional lattice bodies have a surface area of at least about  $30 \text{ m}^2/\text{g}$ , preferably at least about  $50 \text{ m}^2/\text{g}$ , and more preferably at least about  $100 \text{ m}^2/\text{g}$ . In particularly preferred embodiments, the surface area is at least about  $150 \text{ m}^2/\text{g}$ , more preferably at least about  $200 \text{ m}^2/\text{g}$ , and most preferably at least about  $300 \text{ m}^2/\text{g}$ .

The open-celled nature of the porous bodies of this invention can be further characterized in part by pore volume and pore diameter.

The present porous bodies have a pore volume of at least about  $1 \text{ cm}^3/\text{g}$ , preferably at least about  $1.5 \text{ cm}^3/\text{g}$ , and more preferably at least about  $2.0 \text{ cm}^3/\text{g}$ . In particularly preferred embodiments, the pore volume is at least about  $2.5 \text{ cm}^3/\text{g}$ , more preferably at least about  $3.0 \text{ cm}^3/\text{g}$ , and most preferably at least about  $4.0 \text{ cm}^3/\text{g}$ .

The pore diameter can vary substantially to achieve a given pore volume. Generally, the open-celled lattice structure of the porous bodies have an average pore diameter of at least about 50 Angstroms (A). In preferred embodiments, the average pore diameter is at least about 100 A, and more preferably at least about 200 A. In particularly preferred embodiments, the average pore diameter is at least about 250 A, preferably at least about 300 A, and most preferably at least about 350 A. In alternatively preferred embodiments, the average pore diameter ranges from about 50 A to about 500 A. In other embodiments, the average pore diameter is preferably less than about 1000 Angstroms, more preferably less than about 700 Angstroms, and most preferably about 100 to about 400 Angstroms.

In alternative embodiments of the invention, the average pore diameter of the porous bodies can be varied to accommodate specific

applications or screen different materials. For example, in preferred embodiments of the invention one can use articles having an average pore diameter of about 150 to 400A to entrap or immobilize a specific molecule such as an enzyme within the pores of a shaped body. For other applications, such as forming insulation materials from materials of this invention, a relatively small pore (10 to 150 A) may be desired. For applications in which rapid diffusion is important, a relatively large pore diameter may be desired.

One method for controlling the average pore diameter of the present porous bodies involves changing their density as discussed further below. It is important to note that with decreasing density of the porous bodies, their average pore diameter tends to increase. Alternatively, the pore diameter can be controlled by employing a "ghost" mold or imprint technique. The "ghost mold" or imprint technique involves adding to the gel a material (prior to, during, or after gelation) which can later be removed from the gelled material. The ghost material leaves voids when removed. It can be removed by conventional techniques known in the art, such as dissolution or chemical etching.

In spite of their relatively low density, the bodies and articles formed therefrom possess beneficial strength characteristics. The crosslinked, open-celled 3-dimensional lattice structure is believed to provide much of the strength. The porous bodies have a compressive strength such that the body does not fall apart or collapse when subjected to pressure. The porous bodies of this invention have a relatively low yield. Compressive yield corresponds to the stress-strain curve for a given amount of pressure applied to a material of known dimensions. This curve reflects the amount of compression resulting from the applied pressure. See Sibilia's A Guide to Materials Characterization and Chemical Analysis VCM Publishers 1988, 273-275.

The porous bodies of the present invention have compressive strength equal to or less than 75% yield at 300 psi, preferably equal to or less than 50% yield at 300 psi, more preferably equal to or less than 25% yield at 300 psi, and most preferably equal to or less than about 10% yield at 300 psi. In alternative embodiments, the compressive strength is equal to or less than about 10% yield at 1000 psi.

In other preferred embodiments, the porous bodies have compressive strength equal to or less than 10% yield at 10 psi, more preferably equal to or less than 10% yield at 14 psi, and most preferably



equal to or less than 10% yield at 18 psi.

The polymers suitable for the present invention are hydroxyl group-containing natural and synthetic polymers and other synthetic polymers that form hydrogels when solubilized in water or other aqueous solvents, such as aqueous acid or base solutions, and mixtures of water and organic solvents.

Suitable hydroxyl group-containing polymers include natural polymers such as polysaccharides, e.g. alginates, gums, carrageenan, starch, dextrans, chitosan and agar, proteins, e.g. gelatins, casein and collagen; synthetic polymers, e.g. polyvinyl alcohols, vinyl alcohol copolymers and starch/acrylate copolymers; and mixtures and copolymers thereof. Alginate is the general name given to alginic acid and its salts. Alginates are composed of D-mannosyluronic acid and L-gluopyranosyluronic acid residues, and are commercially harvested from seaweeds. Illustrative of suitable alginates are the alkali metal salts of alginic acid, and most preferred is sodium alginate. Gums are polysaccharides extracted from plants, and illustrative of suitable gums are guar gum and locust bean gum. Carrageenan is a colloid extracted from carrageen, and dextrans are polymers of D-glucose. Illustrative of suitable vinyl alcohol polymers are saponified polyvinyl acetate, preferably, having at least about 70 mol% of the acetate group hydrolyzed to be easily soluble in water, and suitable vinyl alcohol copolymers include vinyl alcohol/ethylenimine copolymers and vinyl alcohol/acrylate copolymers.

Other synthetic hydrogel polymers suitable for the present invention include acrylate polymers, polyalkylene amides, polyalkylenimides, polyacrylamides, and mixtures and copolymers thereof. Illustrative of suitable acrylate polymers are monovalent, e.g.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Cs}^+$ , or divalent, e.g.  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Sr}^{+2}$ ,  $\text{Ba}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Cs}^{+2}$ ,  $\text{Pb}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Ni}^{+2}$ , metal salts of polymers derived from acrylic acid, methacrylic acid, methyl methacrylic acid, ethyl methacrylic acid; and polymers derived from hydroxyethyl methacrylate, hydroxyethoxyethyl methacrylate, methoxyethyl methacrylate, methoxyethoxyethyl methacrylate, aminoethyl methacrylate propylene, and glycol methacrylate. Suitable polyalkylenimides include polyethylenimide and the like.

The starting concentration of the hydrogel polymer directly affects the density of the porous bodies. As the concentration of the polymer in the solution increases, the density of the porous body increases. An effective amount of gel-forming polymer is used. An "effective" amount is

in the range of polymer concentrations between the minimum concentration which is high enough to form a gel and the maximum concentration which is low enough to be completely soluble in a gelling solvent. The effective amount of each polymer will vary with the selected density of the porous body. In general, the suitable concentration of the polymer for the present invention is between about 0.02% to about 15%, preferably between about 0.5% to about 12%, and more preferably between about 1% to about 10%.

In order to set or coagulate the polymer solution, hereinafter sometimes also referred to as "pregel", it may be necessary to utilize a gelling agent. Some gel-forming polymers do not require gelling agent, as discussed further below. In general, the polymer solution is exposed to an aqueous solution of an effective amount of gelling agent. The effective amount as used in this connection is the amount of gelling agent which is sufficient to set or coagulate the polymer solution such that its shape is maintained. Appropriate kinds and amounts of gelling agent will depend on the polymer. The gelling agents are well known in the art, and each gel can be prepared by conventional techniques known in the art.

Gelling of the polymer solution takes place over time. The amount of time required depends on the diffusion rate of the gelling agent. The gel's viscosity, which depends on the polymer concentration, generally dictates the length of time needed for the movement of the gelling agent throughout the gel. The higher the concentration of polymer, the longer the required diffusion time. Gelling may also involve a molecular rearrangement of the polymer. To some extent the re-arrangement will occur simultaneously with the diffusion of the gelling agent through the gel, but it may also continue after complete diffusion of the gelling agent. It is believed that without diffusion of the gelling agent throughout the gel, shrinkage or collapse of the gel can occur during the downstream process steps of forming the porous bodies. With the onset of shrinkage, density may increase (as surface area decreases) to a point above a desired level.

The selection of gelling agent depends on the polymer utilized. The gelling agent can be any agent which is reactive with the polymer to set or coagulate the pregel. For alginate, an inorganic or organic cationic material is used to ionically bond the carboxylic acid moieties of the alginate polymer strands. Dicationic or polycationic materials are preferred for their ability to ionically bond the carboxylic acid moieties of two adjacent polymer strands. Sodium alginate can also be gelled using

organic acids or inorganic materials, such as di- or polycationic metals. The organic acids used for gelling alginate, e.g. sodium alginate, can vary widely. Illustrative of such acids are acetic acid, propanoic acid, butanoic acid, benzoic acid, oxalic acid, malonic acid, succinic acid adipic acid, glutaric acid, maleic acid, phthalic acids and derivatives thereof. Preferably, a dicationic metal or dicarboxylic acid is employed in order to link two strands of the polymer together. Suitable cationic ions include ionic forms of and of the following: Al, Ba, Ca, Mg, Sr, Cr, Cu, Fe, Mn, and Zn. Most of the transition metals in the cationic form of  $X^{2+}$  or more can also be employed. Preferably, the cationic metal is a cationic form of Ca, Ba or Cu.

For gums, gelling agents including sodium borate, inorganic acids, organic acids, such as boric acid, and bases are suitable.

Other polymers such as agar, carrageenan, gelatins and casein do not require any additional gelling agent, since they can be gelled by a heat treatment. The pregel solution is heated to a temperature high enough to melt the polymers, followed by cooling to form a gel. For example, an aqueous agar solution will form a gel upon heating to at least 80°C and followed by cooling until gelation occurs.

Polyvinyl alcohol and starch/acrylate copolymers also do not require any agents or additional processes to form gels. They form gels when their aqueous solutions are exposed to an appropriate crosslinking solvent, such as acetone.

Rapid cooling is an alternative to using a gelling agent. This process may be used in addition to treatment with gelling agent or any other gelling technique. The rapid cooling technique involves forming a pregel or gel and dropping the pregel or gel into a solvent bath which has been cooled to a temperature at which the gelling solvent does not freeze, but at which the polymer coagulates. For hydrogel materials, generally, water alone is not suitable as a gelling solvent for the rapid cooling technique since water will freeze and will not diffuse out. Hence, a water/organic solvent mixture is used. In the case of alginate, a water/ethylene glycol (having at least about 25% ethylene glycol or organic solvent) can be used as the gelling solvent. The pregel or gel is then placed in a cooled bath of acetone, which then replaces the water/ethylene glycol solvent.

The gels can be fabricated into any desired shape. Shaping may be carried out by any conventional method known in the art. A polymer

solution can be placed in a mold of any desired shape and then gelled in the mold. For example, a layer of a polymer solution can be placed on a flat surface to form a sheet; a polymer solution can be expressed through an aperture to form a filament fiber or tube, or it can be dripped into a gelling solvent to form granules. Any desired configuration (tubes, cubes, rectangular shapes, sphere, such as beads, pellets, sheets, which may be in the form of membrane) can thus be obtained. In accordance with the present invention, the set or coagulated gels are further subjected to a crosslinking process to increase their physical strength and to preserve the porous structure of the gels.

The gels are prepared for crosslinking by replacing the initial gelling solvent, i.e., water, with a crosslinking solvent. The gelling solvent can be replaced directly with a crosslinking solvent. Alternatively, if the crosslinking solvent is not miscible with the gelling solvent, one or more of intermediate solvents may be utilized. A suitable intermediate solvent is miscible with both gelling solvent and crosslinking solvent. The crosslinking solvent should also be non-reactive with the polymer and the crosslinking agent.

In general, the surface tension of the crosslinking solvent can be less than, greater than, or equal to the surface tension of the gelling solvent. Preferably, the crosslinking solvent has a surface tension substantially equal to the gelling solvent. This would obviate the necessity for solvent exchanges over a concentration gradient as discussed, *infra*. In alternative embodiments, the crosslinking solvent has a surface tension which is less than the gelling solvent. In such embodiments, the crosslinking solvent may have a surface tension which is less than or greater than that of the intermediate solvent. In more preferred embodiments, the crosslinking solvent has a surface tension which is less than about 75 dynes/cm. In further preferred embodiments, the crosslinking agent has a surface tension equal to or less than about 50 dynes/cm. In particularly preferred embodiments, the crosslinking solvent has a surface tension equal to or less than about 40 dynes/cm. In more particularly preferred embodiments, the crosslinking solvent has a surface tension equal to or less than about 30 dynes/cm.

Illustrative of solvents useful for the present invention are acetone, chloroform, dimethyl sulfoxide, toluene, pyridine, and xylene. In many of the preferred embodiments, the crosslinking solvent is an aprotic organic solvent.

In general, the gelling solvent should be substantially, if not completely, removed from the gel prior to crosslinking if the selected crosslinking agent is reactive with the gelling solvent, as the reaction between the gelling solvent and crosslinking agent tends to diminish the crosslinks. For example, the water in a hydrogel polymer will react with a crosslinking agent such as tolylene diisocyanate (TDI). Replacement of the gelling solvent with a crosslinking solvent is generally referred to herein as a solvent exchange step. The actual exchange to the crosslinking solvent from the initial gelling solvent may comprise one or more exchanges of the gelling solvent with an intermediate solvent or solvents prior to replacing the intermediate solvent with the crosslinking solvent.

Preferably, the solvent exchange process comprises replacing the initial gelling solvent with an intermediate solvent of low surface tension, e.g. acetone. The intermediate solvent is selected such that is miscible with both the gelling solvent and with the subsequent intermediate solvent or the crosslinking solvent. Preferably, the intermediate solvent has a surface tension which is lower than that of the gelling solvent. In more preferred embodiments, the intermediate solvent has a surface tension of less than about 75 dynes/cm. In further preferred embodiments, the intermediate solvent has a surface tension equal to or less than about 50 dynes/cm. In particularly preferred embodiments, the intermediate solvent has a surface tension equal to or less than about 40 dynes/cm. In more particularly preferred embodiments, the intermediate solvent has a surface tension which is equal to or less than about 30 dynes/cm.

It is noted that if the crosslinking solvent has a surface tension greater than that of the gelling solvent and an intermediate solvent is used, then the intermediate solvent preferably has a surface tension which is less than the surface tension of the crosslinking solvent and greater than the surface tension of the gelling solvent.

If more than one intermediate solvent is used, then the intermediate solvent need only be miscible with the prior and subsequently used solvents. For example, water can first be exchanged with acetone, which is miscible both with water and with a subsequent crosslinking solvent such as toluene. Acetone is one of the preferred intermediate solvents for several reasons. Acetone is readily available and is relatively innocuous; it is also soluble in water and toluene. Other suitable intermediate solvents which may be used include alcohols, e.g. methanol, ethanol, propanol, and butanol; esters, e.g. methyl and ethyl acetate; ketones, e.g. methyl ethyl

ketone; and others such as dimethyl sulfoxide, dimethylformamide, methylene chloride, ethylene chloride, tetrahydrofuran, dioxane, and the like.

As is known in the art, the pores of porous gels derived from hydrogel polymers collapse to form dense solids having a limited porosity when the gelling solvent is removed, i.e., when dehydrated. In addition, it has been found that when the gelling solvent is abruptly replaced with a crosslinking solvent having substantially different surface tension and polar characteristic, a large portion of the pores of the gels, especially fine pores, collapse to form less porous gels. The collapse of the pores not only significantly decreases the surface area and increase the density of the porous bodies, but also reduced their dimensional stability and physical strength. The collapsed pores prevent access of the crosslinking agent, resulting in uncrosslinked portions in the gel, which are free to swell and shrink.

In order to maintain the porous gel structure without causing shrinkage or collapse of the gel upon removal of the gelling solvent, care must be taken when replacing the gelling solvent with an intermediate solvent. Often, the use of a number of gradual solvent exchanges may be beneficial, using the same intermediate solvent at increasing concentrations. Such solvent exchange is herein referred to as solvent exchange over a concentration gradient. The concentration gradient is used to stepwise decrease the surface tension of the liquid within the gel. An effective concentration gradient is an interval of changes in concentration of intermediate or crosslinking solvent which prevents significant collapse of the gel structure and avoids substantial shrinkage of the gel. In general, though not necessarily, at least one solvent exchange is performed; many of the preferred embodiments employ more than one solvent exchanges. Desirably, the number of steps used and the amount organic waste generated in each batch of exchanges should be minimized. Intermediate waste can be reused, redistilled, or separated to recover the solvents.

For each solvent exchange step, sufficient time should be allowed for the replacement solvent to reach equilibrium. Equilibrium is the point at which the concentration of the replacement solvent inside the gel is in equilibrium with the concentration of the replacement solvent at the outer surface of the gel.

The intermediate solvents are usually a mixture of the intermediate

solvent and the gelling solvent until 100% intermediate solvent is exchanged. The initial concentration of intermediate solvent (or crosslinking solvent, if no intermediate solvent is used), may contain from about 5 to about 25 volume % of the intermediate solvent, and thereafter  
5 the solvent exchanges over the concentration gradient can take place in increasing intervals of 10 volume % or higher.

In preferred embodiments, the intermediate solvent is initially employed in a concentration ranging from about 10 to 25 volume % and the concentration is then stepped up in intervals of from about 15 to about  
10 25 volume %. The incremental increases of from about 20 to about 25 volume % are particularly preferred to minimize the number of solvent exchanges.

Once a substantially complete exchange of intermediate solvent for the initial gelling solvent has taken place, the intermediate solvent can  
15 generally be exposed directly to 100% of the crosslinking solvent. Although it is theorized that for most hydrogel polymers no gradient is required for the exchange from the intermediate solvent to the crosslinking solvent, there may be a situation where a concentration gradient is used for the exchange of an intermediate solvent and a crosslinking solvent.

20 Other known dehydration techniques may be used to prepare the gel for crosslinking. These may be used in addition to or instead of the solvent exchange processes. Sometimes it may be preferable to perform at least one solvent exchange in connection with such techniques. Illustrative of such alternate techniques are freeze-drying, supercritical fluid  
25 extraction, and spray drying. Freeze-drying is advantageous since a solvent exchange procedure should not be necessary. On the other hand, a supercritical fluid extraction can also be beneficial since water can be exchanged by this method, with or without the need for intermediate solvent exchanges.

30 Freeze-drying is a well-known procedure which is frequently used in the food industry. The material to be freeze-dried is first cooled to below the freezing point of the solvent, followed by vacuum drying, as known in the art. The resulting freeze-dried hydrogel structure is directly placed in a crosslinking solvent to be crosslinked. Because the freeze  
35 drying process may not well preserve the porous gel structure, it may be necessary to add surfactants, elastomeric additives, or polyols to the pregel composition to prevent the collapse of pores during the freeze-drying process.

Super-critical fluid extraction involves extractions of the gelling solvent or intermediate solvent at high pressure using supercritical CO<sub>2</sub> in the liquid phase. Supercritical CO<sub>2</sub> is non-polar and can replace the solvent present in the gel. When the pressure is released, the CO<sub>2</sub> evaporates from the porous material. This technique can be used in a fashion analogous to that which has been described for the preparation of inorganic aerogels.

Following freeze-drying or supercritical extraction, the dried material is exposed to a crosslinking agent, which can be provided in solution or in the gas phase, to form a crosslinked porous body. The solvent for the crosslinking agent can vary widely. Such a solvent or gas acts as a carrier vehicle for the crosslinking agent. Obviously, the carrier vehicle should be inert to the gel material and capable of solubilizing the crosslinking agent. The supercritical fluid extraction method may be a preferable procedure for making materials of very low density materials, i.e. less than about 0.05 g/cm<sup>3</sup>.

The choice of crosslinking agent will vary with the polymer, and the amount of crosslinking agent will vary with the amount of polymer present in the gel and the amount of crosslinking desired. The crosslinking agent must be reactive with the functional groups present in the polymer. The polymers suitable for use in the present invention have a variety of functional groups such as -OOH, -OSO<sub>3</sub>, and -NH<sub>2</sub> on their polymer backbone, as well as hydroxyl functional group. Of these groups, the hydroxyl group is preferably targeted for the crosslinking process. The degree of crosslinkage can be varied to suit the needs of each application. The novel gradient solvent exchange process of the present invention that prevents the collapse of the gel pores can facilitate up to 100% crosslinking of all available functional groups present on the surface of the porous gels. The porous bodies of the present invention that are highly crosslinked exhibit high dimensional stability, minimal swellability, and excellent chemical integrity even when exposed to different solvents. Preferably, up to 75% of the functional groups of the hydrogel polymer are crosslinked; more preferably, up to 85% are crosslinked; and most preferably, up to 100% of at least one functional group of the hydrogel polymer is crosslinked. Since, as is known in the art, the maximum molar concentration of available functionalities can be empirically calculated for a given starting concentration of each selected polymer, the approximate amount of crosslinking agent needed to accomplish the desired level of



crosslinkage can easily be determined.

A large number of well-known chemical crosslinking agents are available for use in the crosslinking step. Illustrative of suitable crosslinking agents are diamines and polyamines that crosslink the hydroxyl and/or carboxylic moieties along the hydrogel polymer backbone. For the purposes of this invention, diisocyanate compounds are preferred. The diisocyanate compounds can be aliphatic, cycloaliphatic, or aromatic. Aromatic diisocyanates, such as 2,4-tolylene diisocyanate, 4,4-diphenylmethane diisocyanate, and 1,4-phenylene diisocyanate, are exemplary of preferred embodiments. Other suitable agents for crosslinking the hydroxyl moiety include, for example, diacid halides, such as halide salts of adipic acid, glutaric acid or succinic acid, diepoxides, epichlorohydrin, aldehydes, dialdehydes, trimetaphosphates, vinyl sulfones, trimethylolmelamine, melamine-formaldehyde, urea-formaldehyde systems and di-halogenated aliphatics. Specific examples of such compounds include bis(hydroxymethyl)ethylene urea, N,N'-methylenebisacryl-amide, and 1,3,5-trichloro- and 1,3,5-triacryl s-triazine.

When the hydrogel polymer used is guar gum, the preferred crosslinking agents are borates such as sodium tetraborate or borax; boric acid; oxyanionic species such as aluminates and silicates; and polyvalent oxyanionic species such as arsenates, phosphates, and chromates. It is known that boric acid and borates rapidly form very stable complexes with polyols and alpha-hydroxy carboxylic acids. Other useful borates include potassium borate ( $\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$ ), calcium borates ( $\text{CaB}_2\text{O}_4$ )( $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$ ),  $\text{Mg}_7\text{Cl}_2\text{B}_{16}\text{O}_{30}$ , and non-borax sodium borates ( $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ ). Useful aluminates include aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ) while useful silicates include sodium silicate, varying in composition from  $\text{Na}_2\text{O} \cdot 3.75\text{SiO}_2$  to  $2\text{Na}_2\text{O} \cdot \text{SiO}_2$  with various water content. Useful arsenates include arsenic pentoxide, arsenic acid, sodium arsenate, and pyroarsenate while useful phosphates include orthophosphates, sodium phosphate, ammonium phosphate, condensed phosphates, and polyphosphates. Useful chromates include sodium or potassium dichromate or chromium trioxide. Inorganic and organic cations may also be added to a guar-borate gel in order to produce a stiffer gel. Useful cations include calcium ion such as from calcium chloride, amines such as melamine, polyamine(imine) polymers, and polyethyleneimine. The more preferred crosslinking agents for guar gum are sodium tetraborate, boric acid, and  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  (borax) while the most preferred crosslinking

agent for guar gum is sodium tetraborate.

The crosslinking process takes place over time, and the amount of time required for crosslinking depends on the diffusion of the crosslinking agent throughout the gel. The crosslinking process may be conducted at  
5 any temperature above the freezing point and below the boiling point of the crosslinking solvent. Preferably, the crosslinking process is conducted at an elevated temperature below the boiling point of the crosslinking solvent in order to expedite the process.

Upon completion of the crosslinking process, the crosslinking  
10 solvent is removed from the gel bodies by a variety of conventional techniques, such as draining the liquid from the solid crosslinked product. Evaporation under vacuum is another suitable technique. Suitably, the solid crosslinked material is then dried under reduced pressure at a temperature of at least 20°C to evaporate leftover solvents or volatile  
15 crosslinking agents from the crosslinked gel bodies.

Pore controlling agents such as surfactants, emulsifiers, drying-control chemical agents, elastomeric additives, polyols, and organic and inorganic chaotrophic agents may be used in the present invention. Any material which maximizes pore volume per gram of bulk and minimizes  
20 average pore diameter may be used. Useful commercially available surfactants include biological detergents such as dimethyldioctadecylammonium bromide, the triton series of surfactants such as Triton B, N-101, X-100, X-100 reduced, X-114, and X-405. Other useful surfactants include fluorochemical surfactants such as FC-  
25 171, FC-120, FC-430, and FC-135. Useful commercially available emulsifiers include polyoxyethylated vegetable oils, fatty acids and alcohols, tridecyloxopoly(ethyleneoxy)ethanols, ethoxylated amines, sorbitan, ethoxylated sorbitan esters, amine oxides, sulfated fatty alcohols, and cationic surfactants. Useful commercially available drying-control  
30 chemical agents include organic acids, formamide, and polyols such as glycerol and propanediol. Useful commercially available elastomeric additives include styrene-butadiene copolymer, polychloroprene, cis-1,4-polyisoprene, ethylene-propylene terpolymers, silicone, and uncrosslinked polyolefins. The amount of pore controlling agent used is preferably at  
35 least about 1 part per million, and more preferably, 1 part per million to about 5 percent by weight of the starting gel.

The present porous bodies exhibit numerous beneficial properties including low density and high surface area as well as high pore volume

and excellent strength characteristics. In addition, the porous bodies have excellent dimensional stability even after thorough dehydration and rehydration, especially at high levels of crosslinkage in such levels that are not possible to accomplish using the prior art solvent exchange processes.

5 The numerous beneficial properties of the bodies provide a material with many uses, such as active-agent support materials, fillers, absorbents, adsorbents, filters, fibers, membranes and many other applications.

A principal advantage of the porous bodies of this invention and articles formed therefrom is the diversity of chemical modification which  
10 can be performed on the gel-forming prior to, during, or after isolating the open-celled porous cross-linked body. The above-mentioned functional groups present in polymers suitable for use in the present invention can be chemically modified by employing conventional procedures. The number of functional groups available for chemical modification depends on the  
15 number of functional groups which have been involved in the crosslinking. With less crosslinking, more functional groups will be available for chemical modification. Alginic acid contains a substantial number of carboxyl groups, for example, which are easily derivatized by numerous reagents. Even if one crosslinks these materials using hydroxyl-specific  
20 reagents such as diisocyanates, sufficient free hydroxyls can survive the process intact and should be accessible for further reaction.

The numerous modifications which can be performed on the functional groups of a hydrogel polymer make the range of applications for the porous bodies and articles of this invention almost endless. Suitable  
25 uses include storage and transport of chemicals; support applications, e.g. catalytic reactions or filter media; and insulation and separation applications. If the hydrogel polymer used is guar gum, the resulting product is particularly useful for thermal insulation applications and the product may be in the form of a powder or as solid panels or monoliths.

30 The following examples are merely illustrative of our invention and should not be considered limiting in any way.

#### Procedures for Measuring Properties of the Materials

Surface areas were determined by nitrogen adsorption. Samples  
35 were first degassed for 16 hours in a helium atmosphere at 50°C. Adsorption/desorption measurements were made on a Quantasorb sorption systems, a continuous flow gas chromatographic instrument, manufactured by Quantachrome Corp., Syosset, NY. Values reported are based on

by Quantachrome Corp., Syosset, NY. Values reported are based on single point measurements at liquid nitrogen temperature, 78K, and 0.3 partial pressure of nitrogen in helium with a total flow rate of 20 cm<sup>3</sup>/min. The surface areas were calculated using the BET (Brunauer, Emmett and Teller) isotherm following the procedure recommended by the equipment manufacturer.

The particle bulk density, pore volume, and average pore diameter were determined by mercury porosimetry. Samples were first degassed for 16 hours in a helium atmosphere at 50°C. Measurements were made on a Autopore 9210 mercury porosimeter manufactured by Micromeritics, Norcross, GA. Measurements were taken over the pressure range 20 to 60,000 lb/in<sup>2</sup> (138,000 to 410,000,000 Pa) at 60 points with roughly equal logarithmical spacing. Pressures are converted to pore diameters via the Washburn equation where the surface tension of mercury, 485 dyne/cm, and the contact angle, 140°, are assumed. The corresponding pore diameters go from 10 µm to 3.6 nm. The particle bulk density is measured at 20 lb/in<sup>2</sup> (138,000 Pa), and the apparent bulk density is calculated by measuring the volume of a known weight of packed granules having a size range between about 20 and about 40 mesh. The pore volume includes those pores filled as the pressure changes over the range of the experiment. The average pore diameter is defined as four times the ratio of the pore volume to the total pore area, where the pore surface for pores of a given diameter is calculated from the incremental pore volume assuming cylindrical shape. Procedures followed for operation and analysis were those recommended by the manufacturer of the porosimeter.

The procedure used for the determination of compressive properties of the crosslinked materials was in accordance with the ASTM D 1621 - 73 testing procedure.

### EXAMPLE 1

#### 1. PREPARATION OF A POROUS BODY (MATRIX) FROM CROSSLINKED ALGINATE

Five grams of sodium alginate were added to 100 ml distilled water to yield a 5% solution. After addition of the sodium alginate, the solution was allowed to hydrate for 16 hrs. The fully hydrated polymer was then centrifuged to eliminate air bubbles. The viscous solution was exposed to a 0.2M calcium chloride solution to set or coagulate into a gel. Following completion of the setting step, the gel was cut into cubes of about 1 cc

volume and then calcium alginate cubes were then washed thoroughly in water to remove excess calcium chloride and the calcium alginate cubes were exposed to a solution comprised of 25% acetone in distilled water (v/v). After equilibration, the 25% acetone water solution was decanted and replaced with a 50% acetone/water solution. The 50% acetone/water solution was decanted after equilibration and replaced with 75% acetone/water. Following equilibration in this solvent mixture, the solvent mixture was replaced with 100% acetone. The cubes were then equilibrated in 100% toluene, and crosslinked by the addition of 3.3 ml of 2,4-tolylene diisocyanate (TDI). Triethylamine was added as a base catalyst. The solution was heated to 100-110°C, and allowed to react for about 16 hrs. Following crosslinking, the material was washed in fresh toluene and dried in a vacuum oven. The following table lists various physical properties of the final product.

#### PROPERTIES OF THE CROSSLINKED ALGINATE

Apparent Bulk Density	0.164 g/cm <sup>3</sup>
Surface Area	380 m <sup>2</sup> /g
Pore Volume	2.97 cc/g
Average Pore Diameter	365 Angstroms
Compressibility	10% yield at 347 psi

#### Comparative Example 1

#### 20 PREPARATION OF UNCROSSLINKED POROUS BODIES

##### A) Alginate:

Five grams of sodium alginate were added to 100 ml distilled water to yield a 5% solution. After addition of the sodium alginate, the solution was allowed to hydrate for 16 hrs. The fully hydrated polymer was then centrifuged at 2000 rpm for 30 minutes to eliminate air bubbles. The viscous solution was exposed to a 0.2M calcium chloride solution to set or coagulate into a porous gel. Following the completion of the setting procedure, the gel was cut into cubes of about 1 cm<sup>3</sup> volume and then the calcium alginate cubes were washed thoroughly in water to remove excess calcium chloride. The cubes were then freeze dried by transferring the pellets to freeze drying flasks, freezing at -20°C and then lyophilizing for about 12 to 16 hours.

## b) Agar:

Five grams of agar powder were added to 100 ml distilled water, and centrifuged as above to remove air bubbles. Then the aqueous solution was heated to about 90°C until the agar was completely melted.

- 5 The melted agar was cooled to room temperature to form a porous gel. The gel was then cut into cubes and freeze-dried as described above.

## c) Carrageenan:

The procedure outline above for agar was repeated.

10

## d) Guar Gum:

Five grams of guar gum powder were added to 100 ml distilled water, and the fully hydrated polymer was then centrifuged at 2000 rpm for 30 minutes to eliminate air bubbles. The viscous solution was then treated with 5% borax solution (w/v) and allowed to gel overnight. The gelled, porous gum was then cut into cubes and freeze-dried.

15

## e) Locust Bean Gum:

The procedure outline above for guar gum was repeated.

20

The freeze dried test specimens for the above examples were analyzed for their apparent bulk density (ABD) and surface area. The results are shown below.

25

PROPERTIES OF UNCROSSLINKED POROUS BODIES

Sample	ABD (g/cm <sup>3</sup> )	Surface Area (m <sup>2</sup> /g)
Alginate	0.243	20.7
Guar Gum	0.23	1.9
Locust Gum	0.15	2.8
Agar	0.09	4.6
Carrageenan	0.26	5.7

As can be seen from the ABD and surface area data of the uncrosslinked porous bodies, the uncrosslinked bodies have significantly smaller surface area and lower density than that of the crosslinked porous bodies prepared in accordance with the present invention, for example, the porous body of Example 1.

EXAMPLE 2

## OPTIMIZATION OF THE SOLVENT EXCHANGE PROCEDURE

2% calcium alginate gels were prepared in accordance with the procedure outline in Example 1. The water in the gels was replaced with toluene, a crosslinking solvent, using acetone as an intermediate solvent. Prior to replacing the water with toluene or another crosslinking solvent, it is often advantageous to replace the water with an intermediate solvent which is aprotic and has a surface tension less than that of water and above that of the crosslinking solvent. It was observed that abrupt exposure of a gel to high acetone concentrations resulted in partial shrinkage of the gel, which should be avoided to maintain a low density material. In order to minimize the shrinkage of the gel, the maximum step-size increase in concentration of intermediate solvent was determined by making four crosslinked gels using different concentration gradients of the intermediate solvent. For one example, the water of the gel was replaced directly with pure acetone (100%). In the other three samples, concentration gradients of 10%, 25%, and 50% were used. For each gradient, the concentration of acetone in the gel was increased incrementally to 100%, e.g. nine equal incremental steps from 10% acetone in water to reach 100% acetone in the gel. To assess gel shrinkage, the initial pellet diameters of a representative population were measured, and the pellets were then exposed to the next step up in acetone concentration. The pellet diameters were remeasured after a 15 minute equilibration period and the process was repeated until the pellets were in 100% acetone. Finally, the pellets were placed directly into 100% toluene (the crosslinking solvent), or washed further with fresh acetone before exposure to toluene. The results are shown in the Figure 2, which demonstrates an unambiguous relationship between the concentration step-size and the gel shrinkage. Exposing the pellets directly to 100% acetone resulted in a volume reduction of greater than 60%. Taking the acetone concentration to 100% in two steps (50%/step) resulted in less than about 25 % shrinkage. About 24% shrinkage was observed in pellets taken to 100% acetone in four steps (25% step); whereas increasing the acetone to 100% in ten steps (10% each step) resulted in only about 20% shrinkage of the gel. The complete changeover to acetone, therefore, may be effected in as little as four incremental steps (25% acetone/water, 50% acetone/water, 75% acetone/water, 100% acetone). In addition, it was found that the pellets could be exposed directly to 100% toluene with little

additional shrinkage once the pellets were solvent exchanged to 100% acetone.

### EXAMPLE 3

#### PREPARATION OF ULTRA-LOW DENSITY POROUS BODY FROM CROSSLINKED ALGINATE

5 A 0.25% solution of sodium alginate was fully hydrated in 100 ml of distilled water. The hydrated solution (pre-gel) was then transferred to a syringe and centrifuged to eliminate air voids within the gel. The pre-gel was then introduced drop-wise into a solution of 0.2 M calcium chloride,  
10 and the resulting pellets were allowed to coagulate. The calcium solution was then decanted, and the calcium alginate pellets were washed in a large excess of distilled water to remove excess calcium chloride solution. Following the wash step, the pellets were solvent exchanged to toluene and crosslinked with 2,4-TDI, following the procedure outlined in  
15 Example 1. The pellets were then freeze dried by transferring the pellets to freeze drying flasks, freezing at  $-20^{\circ}\text{C}$  and then lyophilizing for about 12 to 16 hours. The density, surface area, and pore characteristics were measured.

#### 20 PROPERTIES OF ULTRA-LOW DENSITY CROSSLINKED ALGINATE

Apparent Bulk Density	$0.042 \text{ g/cm}^3$
Surface Area	$200 \text{ m}^2/\text{g}$
Pore Volume	$2.917 \text{ cc/g}$
Pore Area	$226 \text{ m}^2/\text{g}$
Average Pore Diameter	517 Angstroms

### EXAMPLE 4

#### 25 PREPARATION OF CROSSLINKED ALGINATE USING A QUICK-COOLING TECHNIQUE TO SET THE INITIAL GEL

Fifty milligrams of sodium alginate were added to 10 ml of 58% ethylene glycol in water, and the mixture was allowed to gel. The fully hydrated gel was then extruded dropwise into 100 ml of precooled acetone  
30 ( $-40^{\circ}\text{C}$ , on dry ice). The rapid transition to this temperature caused the alginate gel to become rigid, but the gel did not freeze because of the ethylene glycol in the gel mixture. The extruded pellets were allowed to stir for about 1/2 hour in the cold acetone, and then the wet acetone was



decanted and the pellets were transferred to a 100 ml pear-bottom flask containing 80 ml of pre-cooled, dry acetone, kept under nitrogen. The flask was allowed to warm to about 22°C and then the gel was crosslinked with two additions of molar excess of 2,4-TDI. The final bulk density of the dried material was about 0.028 g/cm<sup>3</sup>.

#### EXAMPLE 5

##### PREPARATION OF CROSSLINKED ALGINATE USING DILUTE ORGANIC ACID AS A GELLING AGENT

A 2% sodium alginate solution (12ml) was extruded dropwise into 200 ml of 10% acetic acid (v/v). The pellets were allowed to set overnight, washed with water to remove excess acetic acid, and then subjected to the solvent exchange and TDI crosslinking procedures described above. The pellets were freeze-dried overnight, as noted in Example 4, and the final bulk density of the unground pellets was about 0.031 g/cm<sup>3</sup>.

Other organic acids capable of gelling the sodium alginate include adipic and formic; however, a simple mineral acid such as HCl had the opposite effect of substantially destroying the gel completely.

#### EXAMPLE 6

##### EFFECT OF INITIAL GEL CONCENTRATION ON THE FINAL DENSITY OF THE CROSSLINKED MATERIAL

The effect of the initial gel concentration on the final density of crosslinked material was determined by preparing a series of gels of increasing concentration, and comparing the densities of the final dried, crosslinked products. Gels were prepared with initial concentrations of 0.25%, 0.5%, 1.0%, and 2.0% (w/v) were prepared. The gels were set as pellets by dropwise introduction into a solution of 0.2 M CaCl<sub>2</sub>, generally as described in Example 5. The calcium alginate pellets were then solvent exchanged and crosslinked with 2,4-TDI as described in Example 1. Following crosslinking, the reaction solution was decanted, and the pellets were dried. The dried materials were then ground to a particle size of less than about 20 mesh and the apparent bulk densities (ABD) were measured. As can be seen in Figure 3, the final ABD of a given material was highly dependent upon the concentration of the starting gel from which it was made. The significance of these findings is that the final density of a material can be controlled by selecting an initial gel concentration which

will yield the desired density.

#### EXAMPLE 7

##### RELATIONSHIP BETWEEN DENSITY AND PORE SIZE OF THE POROUS BODIES FORMED FROM CROSSLINKED GELS

5 Mercury porosimetry was performed on the same four samples described in the preceding example. The intent was to determine whether or not a relationship existed between the final ABD of crosslinked alginate and the average pore diameter of the material. As can be seen in Figure 4, such a relationship does exist. As the apparent bulk density decreases, the  
10 average pore diameter is seen to increase, within the ranges investigated. These results imply one would be able to, within limits, control the pore diameter of the final crosslinked material. For example, if a specific application requires pore diameters in the 200 - 300 angstrom range (ideal for immobilized enzyme supports), then one could process gels of the  
15 appropriate initial concentrations to yield a final product with a final density of about  $0.15 \text{ g/cm}^3$  or greater.

#### EXAMPLE 8

##### RELATIONSHIP BETWEEN DENSITY AND SURFACE AREA OF 20 POROUS BODIES FORMED FROM CROSSLINKED BIOHYDROGELS

The surface area of several crosslinked alginate samples of varying densities was measured in order to determine if there was a definable relationship between surface area and density. The data points arrayed  
25 along the two lines (solid and dashed) represent two families of materials which had different processing conditions. The samples along the solid (lower) line were processed as pellets, and were freeze-dried after crosslinking with 2,4-TDI. The data points along the dotted (upper) line were processed as cubes and were dried in a vacuum oven. As can be  
30 seen in Figure 5, a relationship between ABD and surface area exists, indicating that by careful selection of the initial gel concentration and processing technique, the surface area of the present porous bodies can be controlled to have desired ranges.

#### EXAMPLE 9

##### NATURALLY-DERIVED HYDROGEL POLYMERS

35 Various naturally-derived hydrogels were tested for their ability to form low-density crosslinked materials. The following materials were

tested; Sodium Alginate, Chitosan, Agar, Carrageenan, Locust Bean Gum, Guar Gum, Gum Arabic, Gum Ghatti, Pectin, Tragacanth, and Xanthan Gum. Dissolving Gums Arabic, Ghatti, Tragacanth, and Xanthan in distilled water resulted in the formation of viscous solutions, but no good gelling procedure was found for any of them. Pectin was gelled using the following procedure: To 100 ml distilled water was added 5 g of pectin, 3 g of  $\text{CaCl}_2$ , and 0.2 g of citric acid. The mixture was heated slowly to  $80^\circ\text{C}$ , and allowed to cool to room temperature. The pectin gel that resulted was not sufficiently strong to be useful. 5% Na-alginate solution was set in 0.2 M  $\text{CaCl}_2$ , and 5% chitosan was gelled in dilute acetic acid (Ca. 4% w/w) and then set in 10% NaOH (w/w). 5% mixtures of agar in water and carrageen in water were heated to about  $100^\circ\text{C}$ , and then allowed to cool to set into stiff gels. 5% solutions of guar and locust bean gum were prepared, and then set with sodium borate solution. Following gelling, the gels were sliced into cubes of approximately  $1\text{ cc}^3$  volume. The cubes were then subjected to the solvent exchange and crosslinking procedures described in Example 1, and then dried. To assess the utility, of the various materials, their net shrinkage was measured. Shrinkage was used as a criterion, since as the materials shrink they densify. Therefore, the dimensions of a statistically representative population of the starting cubes ( $n = 5$ ) were measured using a micrometer, and the dimensions were remeasured after the solvent exchange procedure, after the crosslinking procedure, and after the final drying. As can be seen in Figure 6, the chitosan and sodium alginate show superior properties. The agar and carrageenan displayed minimal shrinkage during the solvent exchange procedure. However, upon drying, these two collapsed to a fraction of their initial volumes. The locust bean and guar gum samples collapsed with the initial solvent exchange procedure. The fact that the agar and carrageenan did not collapse during the solvent exchange procedure also makes them viable candidates for other crosslinking procedures.

COMPARATIVE EXAMPLE 2

Using the chitosan crosslinking procedure disclosed in Kokai Patent Publication No. 133143-1986, "Heavy Metal Adsorbing Agent", a sample was prepared.

5 A material was prepared as described in example 1 of this publication. Shrinkage of the material produced using their protocol was used as a guide to assess collapse of the material. The degree of collapse of their material was compared to those values obtained using our procedures in order to determine the relative performance of the two  
10 procedures.

Chitosan, was mixed with dilute acid, such as formic or acetic, to make a gel and then placed in a solution of sodium hydroxide, which coagulates the chitosan to form an opaque, friable material. The coagulated chitosan pellets are placed directly into acetone, and after  
15 washing with fresh acetone, added 2,4- tolylene diisocyanate to effect the crosslinking. The chitosan pellets shrank during the initial exposure to acetone. The initial diameters of 20 pellets were measured using a micrometer, and the pellets were remeasured after drying the pellets. The pellets went from an average initial diameter of 2.27 mm to only 1.457 mm  
20 after drying, a loss of 57.5% in diameter. Using the procedure of our Example 1 procedure, however, the loss was only about 3.3%.

EXAMPLE 10CROSSLINKED GELATIN MATRIX

25 Five grams of gelatin (275 bloom<sup>\*</sup>) were mixed with 100 ml of distilled water and heated to 90 - 100°C with stirring. Upon complete dissolution of the granular gelatin, the solution was allowed to cool to room temperature, thus gelling the proteinaceous material. The gel was then sliced into cubes of approximately 1 cc volume, transferred to a 250  
30 ml round-bottom flask and then subjected to the solvent exchange and crosslinking procedure as described in EXAMPLE 1. The crosslinked product was then washed with fresh toluene, dried in a vacuum oven, and ground to a powder (less than 40 mesh). The table below lists the physical properties of the final material.

35 <sup>\*</sup> -See Mantell Thomas C.L., Water-Soluble Gums, Reinhold Publishing Co. (New York), 1947, pp. 174 and 209.

PROPERTIES OF CROSSLINKED GELATIN

Apparent Bulk Density	0.119 g/cm <sup>3</sup>
Surface Area	110 m <sup>2</sup> /g
Pore Volume	1.31 cm <sup>3</sup> /g
Pore Area	151 m <sup>2</sup> /g
Average Pore Diameter	350 Angstroms

EXAMPLE 11STARCH/ACRYLATE COPOLYMER GEL

5        10 g of Sanwet®, a starch grafted sodium polyacrylate polymer, available from Hoechst-Celanese, was dissolved in 200 ml of distilled water. 100 ml of the solution was added to 500 ml of 50% acetone in water at room temperature, resulting in a coagulated sponge-like gel. After 2 hours, the 50% acetone was decanted and 75% acetone was  
10       added, and then the same process was repeated for 100% acetone. After 1 hour, the gel was broken up with a spatula and the acetone was decanted. The resulting gel is placed in a round bottom flask and 500 ml of fresh 100% acetone was added. Again, after 2 hours the acetone was replaced with fresh 100% acetone. 1 hour thereafter, the acetone was decanted and  
15       replaced with 100% toluene. The toluene was replaced with fresh 100% toluene in 1 hour, and this process was repeated one more time.

The fully solvent exchanged gel suspended in toluene was slowly heated to 80°C. 100µl of TEA was added and a condenser was placed on the flask. 10 minutes later 5.93 ml of TDI added and undisturbed for 3  
20       days. The resulting crosslinked gel was collected and dried in a vacuum oven for 5 hours. The crosslinked, dried gel was determined to have an apparent bulk density of 0.349 g/cm<sup>3</sup>.

EXAMPLE 12Synthetic Hydrogel Polymer Gels

25       Crosslinked porous bodies of synthetic hydrogel polymers, including polyvinyl alcohol, polyethyleneimine, vinylalcohol/ethylenimine copolymers, acrylate polymers, are prepared. The polymers are dissolved in water, gelled and crosslinked by following the procedures outlined in  
30       Example 11. The resulting crosslinked bodies have an apparent bulk density of less than 1.0 g/cm<sup>3</sup>.

EXAMPLE 13Preparation of Low-Density Porous Material From Guar  
Crosslinked With Boric Acid

4 grams of guar gum were added to 100 ml of distilled water and the  
5 powder was dissolved with gentle application of heat. 0.8 grams of boric  
acid were then added and mixed vigorously until as much of the boric acid  
dissolved as was possible. The crosslinked guar was then pressed into a  
cylindrical form while still hot and frozen using dry ice. The frozen  
cylinder was then placed in a lyophilizer and freeze-dried. The final dried  
10 cylinder (5.7 cm diameter by 1.4 cm in height) was weighed, and the piece  
density was determined to be 0.0442 g/cc. This product was stiff, was  
very robust for the low density, and should easily be able to withstand  
atmospheric pressure with minimal compression.

15 This product may be used to form solid panels or monoliths or may  
be ground to be used as a powder.

EXAMPLE 14Preparation of Low-Density Porous Material From Guar  
Crosslinked With Sodium Borate

20 4 grams of guar gum were dissolved in 100 ml of distilled water,  
aided by gentle heating at about 100°C. 1.192 grams of sodium  
tetraborate decahydrate were then added to the guar solution, and the  
mixture was stirred vigorously to evenly distribute the sodium borate. The  
gel, thus formed, was intermittently heated to aid in the dispersal of the  
25 inorganic salt. The crosslinked guar was chopped into irregular pieces of  
about 5 mm in size, and then frozen and freeze-dried as described above.  
The stiff, brittle freeze-dried product was ground to a powder of 20-40  
mesh in size using a Wiley bench mill, and the apparent bulk density  
(A.B.D.) was measured to be 0.046 g/cc. The powder was then ground to  
30 a much finer size using a Trost (Colt Industries) Gem T air impact  
pulverizer. The A.B.D. of this micron sized powder was measured to be  
about 0.115 g/cc, indicating retention of much of the porosity of the  
starting material. The micron sized powder had an average pore diameter  
of 379 Angstroms.

EXAMPLE 15

## Preparation of Crosslinked Guar-Melamine-Formaldehyde Resin

- 2.5 grams of guar gum and 1.94 grams of melamine were mixed well with 100 ml of distilled water, and stirred vigorously with gentle
- 5 heating until an evenly dispersed suspension or solution was achieved. 1 gram of boric acid was then folded into the viscous mixture, upon which a very stiff, ropy, taffy-like material was formed. This mixture was then put in an oven at 135°C for one hour, after which the mixture turned transparent indicating formation of a solution of the various components.
- 10 10 ml of a solution of formaldehyde in water (37% w/w) were then added to the guar/melamine/boric acid solution and the mixture was placed back into the oven at 95°C. Within 30 minutes, a rubbery opaque gel or resin had formed which was not water soluble, indicating covalent crosslinking had occurred. This resin could be air dried without loss of volume. The
- 15 crosslinked gel was then washed exhaustively with water to remove unreacted monomer, and freeze-dried as described above. The dried product was very brittle and had a piece density of 0.049 g/cc.

WHAT IS CLAIMED IS:

1. A crosslinked, highly porous body derived from a water-soluble, hydrogel polymer, said porous body being characterized in that it has an open-celled 3-dimensional lattice structure, a density of less than about 1.0 g/cm<sup>3</sup>, a surface area of equal to or greater than about 30 m<sup>2</sup>/g, a compression strength of equal to or less than about 10% yield at 10 psi, and an average pore diameter of less than about 1000 Angstroms wherein said hydrogel polymer is selected from the group consisting of alginates, gums, starch, dextrans, agar, gelatins, casein, collagen, polyvinyl alcohol, polyethylenimine, acrylate polymers, starch/acrylate copolymers, and mixtures and copolymers thereof.
2. The porous body of claim 1, wherein said body is derived from guar gum and crosslinked with a crosslinking agent selected from the group consisting of sodium tetraborate, boric acid, and melamine.
3. A solid panel or monolith formed from said crosslinked, highly porous body of claim 1.
4. A powder derived from a water-soluble, hydrogel polymer wherein said powder has an average particle diameter of about 1 to about 10 microns, an average pore diameter of less than about 1000 Angstroms, a density of less than about 1.00 g/cm<sup>3</sup>, and a compression strength of equal to or less than about 10% yield at 10 psi, wherein said hydrogel polymer is selected from the group consisting of alginates, gums, starch, dextrans, agar, gelatins, casein, collagen, polyvinyl alcohol, polyethylenimine, acrylate polymers, starch/acrylate copolymers, and mixtures and copolymers thereof.
5. The powder of claim 4 wherein said powder has an average pore diameter of about 100 to about 400 Angstroms.
6. A process for making a crosslinked, highly porous body comprising:
  - a) dissolving a hydrogel polymer in a gelling solvent, said hydrogel polymer selected from the group consisting of alginates, gums, starch, dextrans, agar, gelatins, casein, collagen, polyvinyl alcohol,



polyethylenimine, acrylate polymers, starch/acrylate copolymers, and mixtures and copolymers thereof,

b) forming a gel from the dissolved polymer solution into a desired configuration,

5 c) gradually replacing said gelling solvent with a crosslinking solvent by employing a concentration gradient solvent exchange process,

d) adding a crosslinking agent to crosslink said gel, and

10 e) isolating the crosslinked gel from said crosslinking solvent, wherein said porous body is characterized in that it has an open-celled 3-dimensional lattice structure, a density of less than about  $1.0 \text{ g/cm}^3$ , a surface area of equal to or greater than about  $30 \text{ m}^2/\text{g}$ , a compression strength of equal to or less than about 10% yield at 10 psi, and an average pore diameter of less than about 1000 Angstroms.

15

7. A crosslinked gel body made in accordance with the process of claim 6.

20 8. The process of claim 6, wherein said concentration gradient solvent exchange process utilizes an intermediate solvent that is miscible to both said gelling solvent and said crosslinking solvent.

25 9. The process of claim 6 wherein said intermediate solvent is selected from the group consisting of alcohols, acetates, ketones, dimethyl sulfoxide, dimethylformamide, methylene chloride, ethylene chloride, tetrahydrofuran, dioxane and the like.

10. A process for making a crosslinked, highly porous body comprising:

30 a) dissolving a hydrogel polymer in a gelling solvent that contains an additive selected from the group consisting of surfactants, elastomeric additives, and polyols, said hydrogel polymer selected from the group consisting of alginates, gums, starch, dextrans, agar, gelatins, casein, collagen, polyvinyl alcohol, polyethylenimine, 35 acrylate polymers, starch/acrylate copolymers, and mixtures and copolymers thereof, b) forming a gel from the dissolved polymer solution into a desired configuration,

- c) freeze-drying said gel,
- d) adding a crosslinking solvent to the freeze-dried gel,
- e) adding a crosslinking agent to said crosslinking solvent, and
- f) isolating the crosslinked gel from said crosslinking solvent,

5 wherein said porous body is characterized in that it has an open-celled 3-dimensional lattice structure, a density of less than about  $1.0 \text{ g/cm}^3$ , a surface area of equal to or greater than about  $30 \text{ m}^2/\text{g}$ , a compression strength of equal to or less than about 10% yield at 10 psi, and an average pore diameter of less than about 1000 Angstroms.

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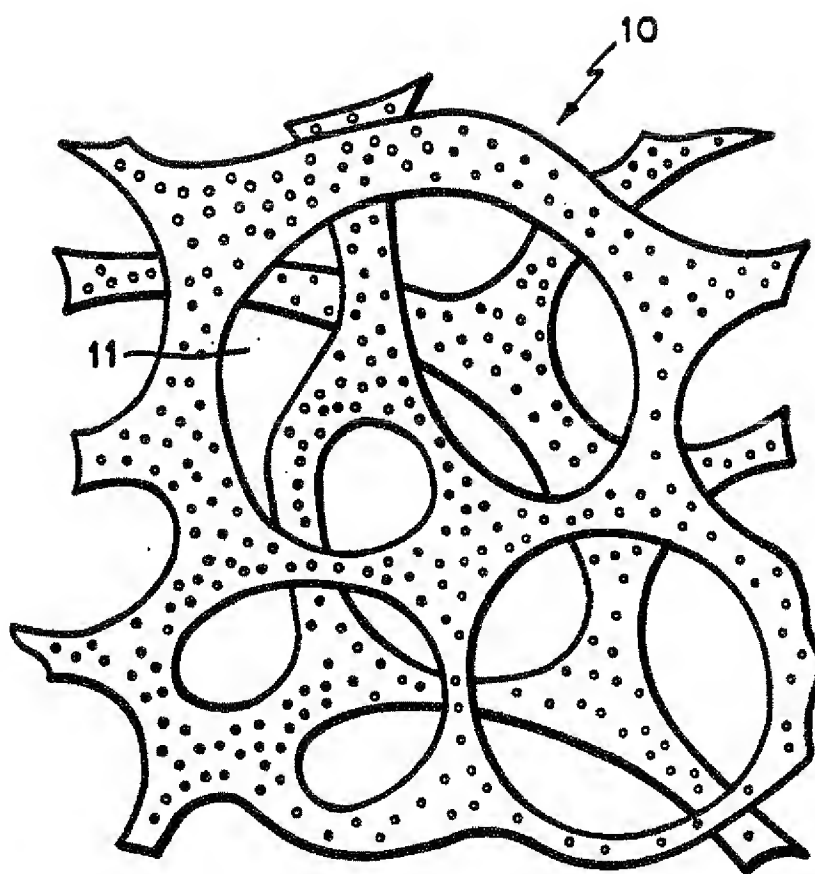


FIGURE 1

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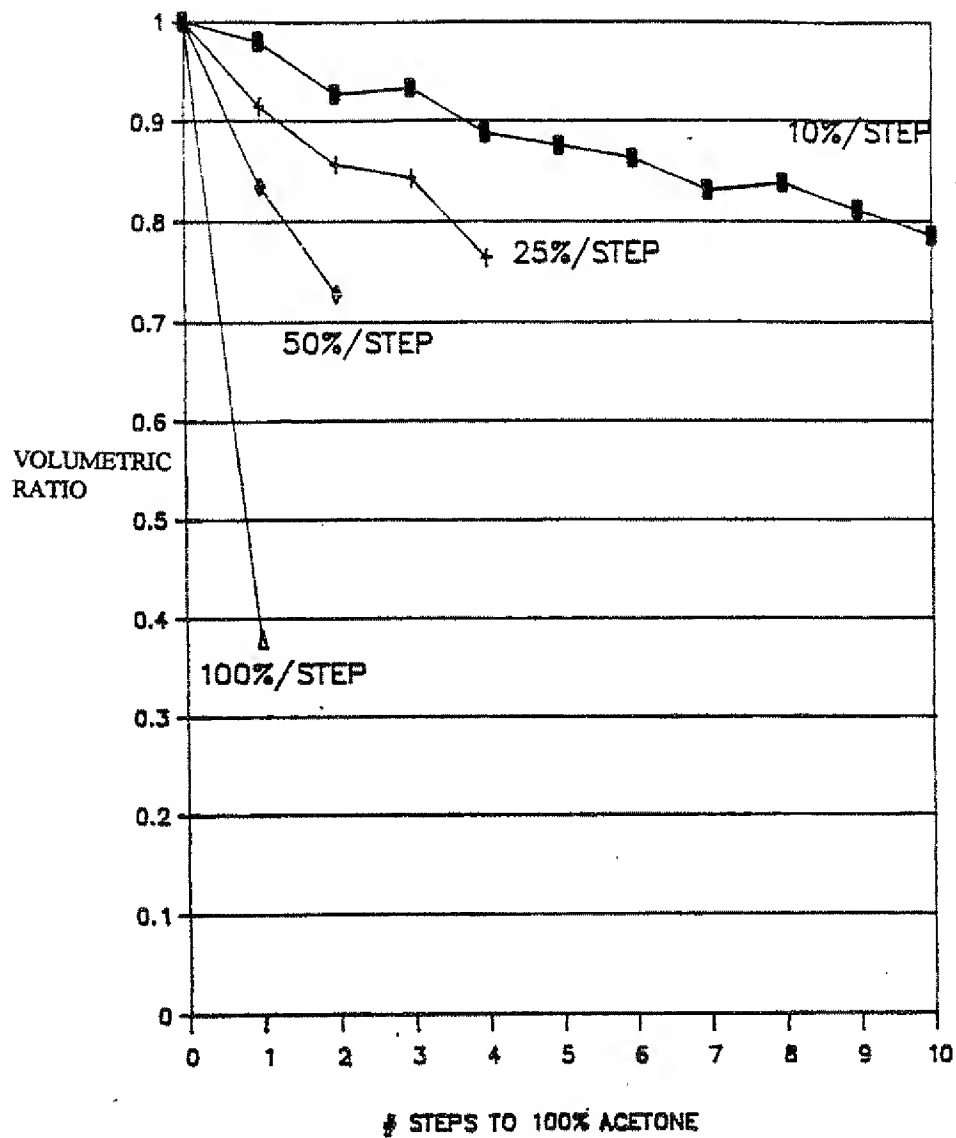


FIGURE 2

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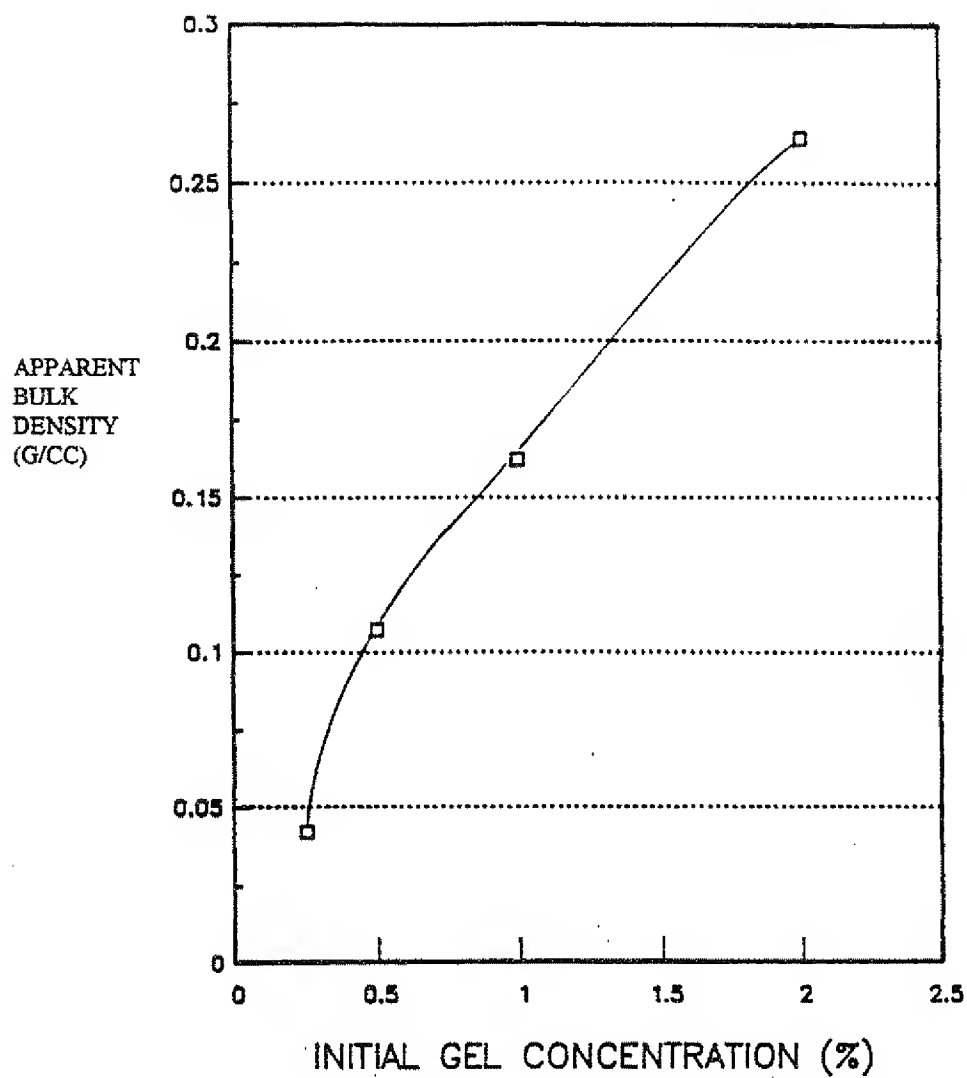


FIGURE 3

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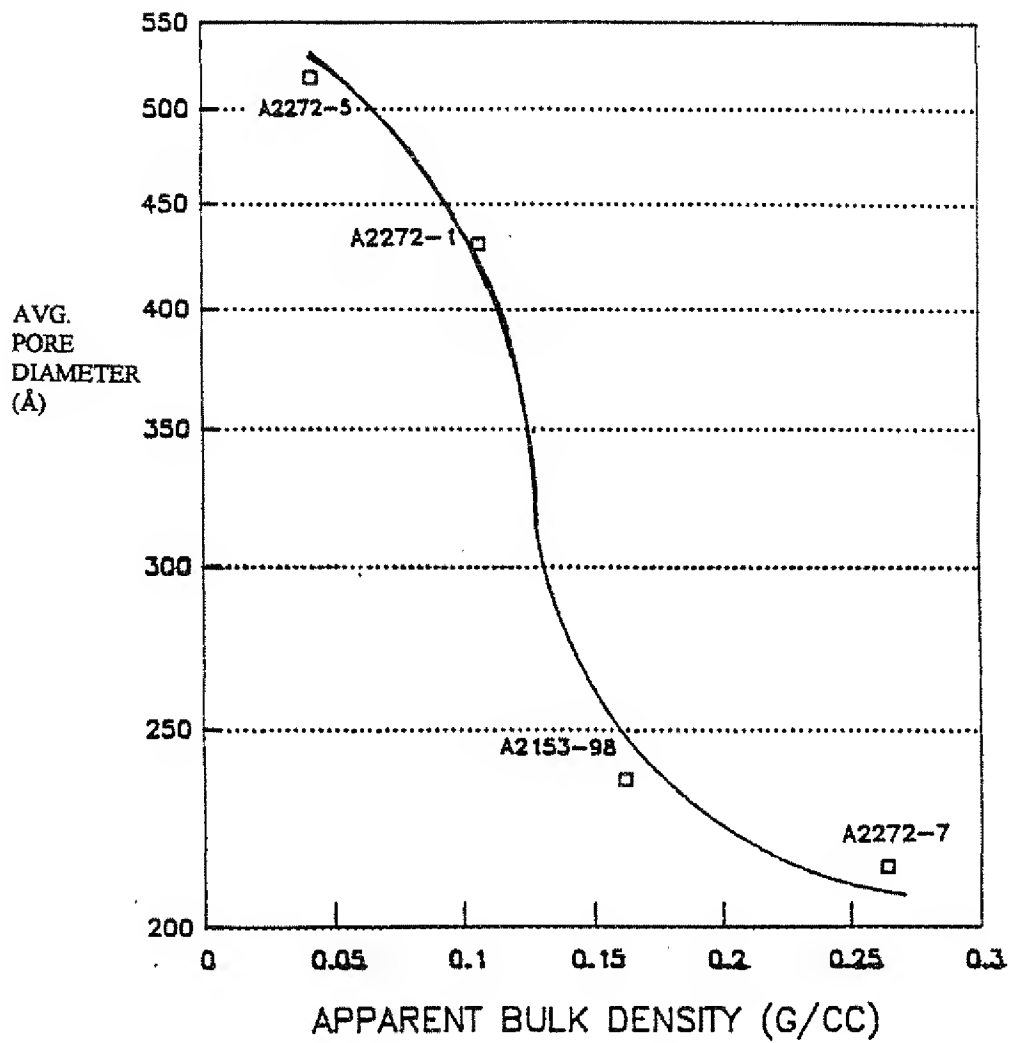


FIGURE 4

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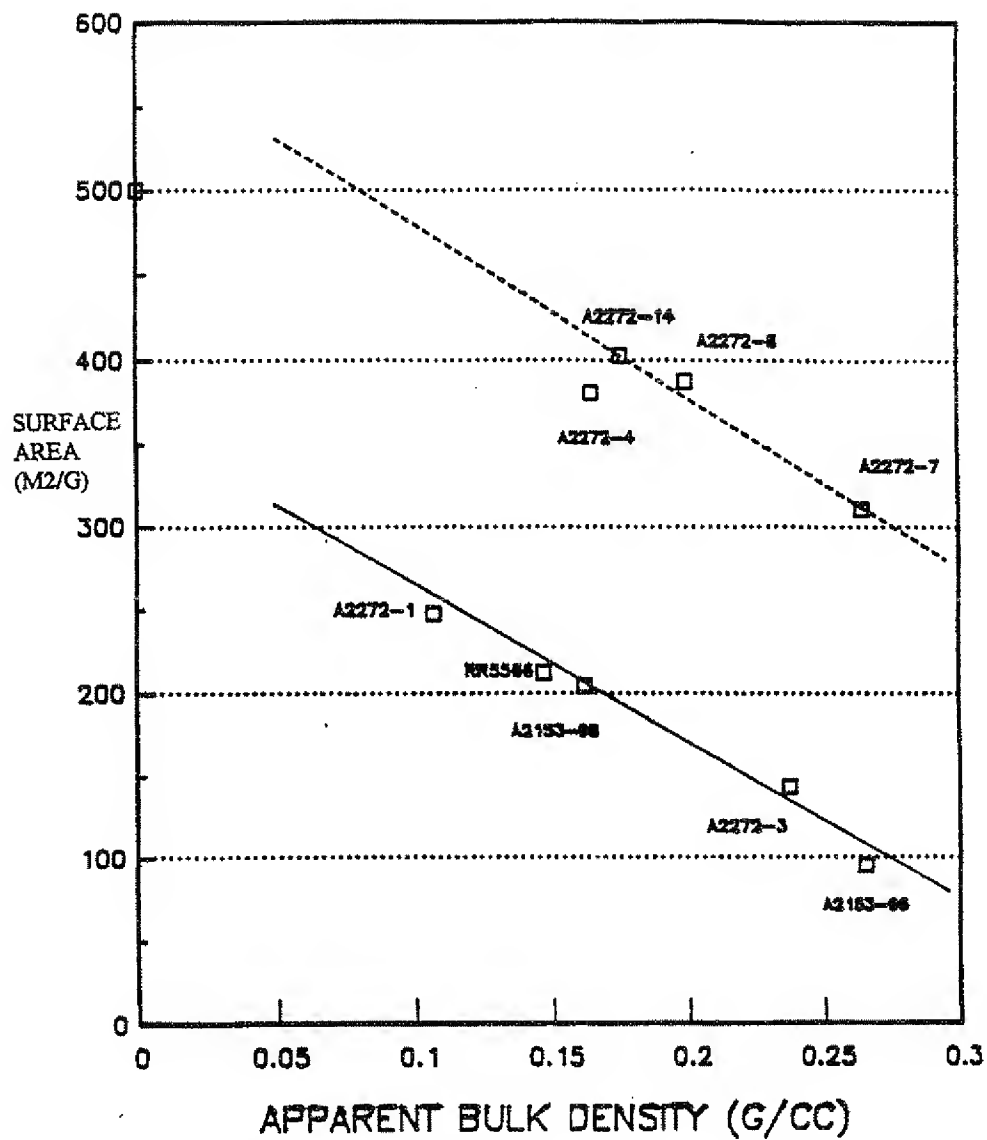


FIGURE 5

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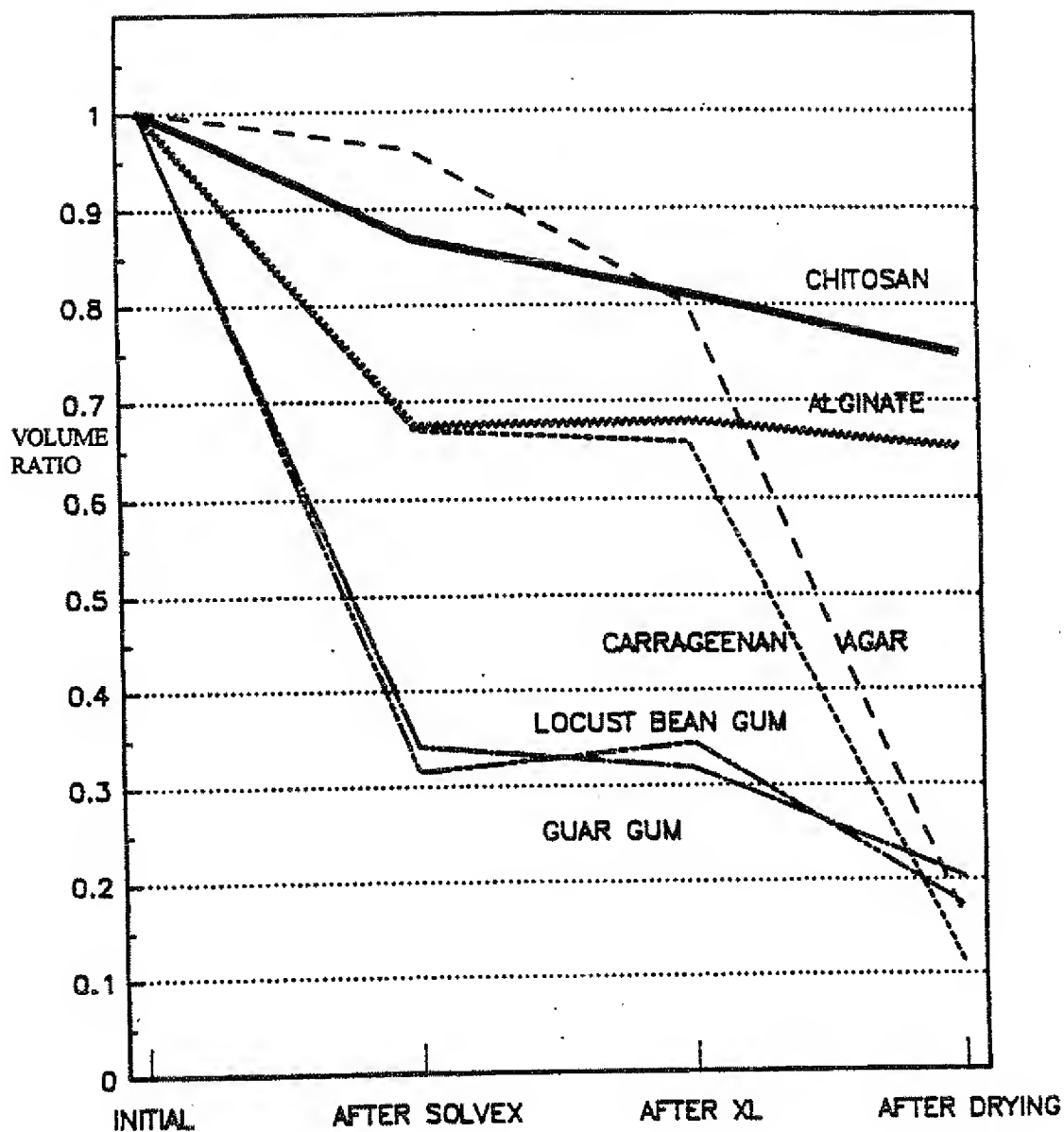


FIGURE 6



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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08J 9/28, 3/12, 3/075</b>	<b>A3</b>	<b>(11) International Publication Number:</b> <b>WO 95/12632</b> <b>(43) International Publication Date:</b> 11 May 1995 (11.05.95)
<b>(21) International Application Number:</b> PCT/US94/12645 <b>(22) International Filing Date:</b> 2 November 1994 (02.11.94) <b>(30) Priority Data:</b> 08/148,110 4 November 1993 (04.11.93) US <b>(71) Applicant:</b> ALLIEDSIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US). <b>(72) Inventors:</b> UNGER, Peter, D.; 36 Terry Drive, Convent Station, NJ 07961 (US). ROHRBACH, Ronald, P.; 430 Cherryville Road, Flemington, NJ 08822 (US). <b>(74) Agent:</b> CRISS, Roger, H.; AlliedSignal Inc., (Attn: C.A. McNally, Law Dept.), 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).		<b>(81) Designated State:</b> JP.  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>  <b>(88) Date of publication of the international search report:</b> 26 May 1995 (26.05.95)
<b>(54) Title:</b> LOW DENSITY MATERIALS HAVING GOOD COMPRESSION STRENGTH AND ARTICLES FORMED THEREFROM		
<b>(57) Abstract</b>  A crosslinked, highly porous body derived from a water-soluble, hydrogel polymer, wherein the porous body is characterized in that it has an open-celled 3-dimensional lattice structure, a density of less than about 1.0 g/cm <sup>3</sup> , a surface area of equal to or greater than about 30 m <sup>2</sup> /g, a compression strength of equal to or less than about 10 % yield at 10 psi, and an average pore diameter of less than about 1000 Angstroms. When the hydrogel polymer used is guar gum, the resulting product is particularly useful for thermal insulation applications.		

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## INTERNATIONAL SEARCH REPORT

Int. Application No.

PCT/US 94/12645

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 6 C08J9/28 C08J3/12 C08J3/075

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## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,93 12877 (ALLIED-SIGNAL INC.) 8 July 1993 see claims 1,3,5,6,14 see page 12, line 6 - page 13, line 23 see page 21, line 26 - page 22, line 32 see page 24, line 31 - page 25, line 17 see examples 1,2,4-11 ---	1,3-10
X	US,A,4 181 649 (MATSUSHITA S. ET AL) 1 January 1980 see claims 1,2,4 see column 3, line 26 - line 34 ---	1,4,5
A	EP,A,0 446 473 (BEIERSDORF AG) 18 September 1991 see claim 1 -----	1

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